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VAPOR ABSORPTION AND CONDUCTIVITY IN POLY(ETHYLENE
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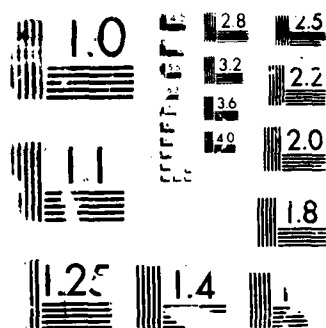
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Vapor Absorption and Conductivity in
Poly(ethylene Oxide)-Salt-Propylene Glycol Films

by

M. M. Nicholson and F. A. Pizzarello

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VAPOR ABSORPTION AND CONDUCTIVITY IN POLY(ETHYLENE OXIDE)-
SALT-PROPYLENE GLYCOL FILMS

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ABSTRACT

The use of propylene glycol (PG) as a plasticizer to increase the conductivities of solid poly(ethylene oxide) (PEO)-salt electrolyte films was investigated. The film conductances were measured at various times during exposure to PG vapor while the absorbed PG was monitored by IR spectroscopy. Spontaneous loss of PG following absorption was observed with PEO-LiBF₄-PG films but not when the salt was LiCl, KCl, or a combination of LiBF₄ and KCl. With the composition (PEO)_{4.1}LiBF₄(KCl)_{0.70}, a conductivity of $4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 23°C was attained.

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The desire for solid-state lithium batteries has motivated extensive research on organic polymer electrolytes during the last ten years. With the battery application foreseen, attention has been focused on aprotic systems, and, for low-rate cells, conductivities as low as $10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$ have been of practical interest. Notable progress in this field has been made by using complexes of simple salts with aliphatic polyethers such as poly(ethylene oxide) (PEO)⁽¹⁾ and with certain polyphosphazenes.⁽²⁾ Solid electrolytes are also of major interest to potential users of electrochromic displays and other electrochemical devices, but higher conductivity is preferred for fast response, and the absence of protons is not a general requirement.

It is now widely recognized that ion transport in the better polymer-salt electrolytes occurs primarily in amorphous regions; hence, a low crystal-to-glass transition temperature is a most desirable characteristic. Pursuing this concept further, some investigators have improved conductivities in polymer-salt systems by introducing a solvent component, or plasticizer.⁽³⁻⁵⁾ Shriver and co-workers used poly(ethylene glycol) (MW 300) to enhance the conductivities of polymer-salt complexes⁽³⁾ and of polymeric ionomers having only one mobile species.⁽⁴⁾ Reed, Geng, and Murray observed improved voltammetric behavior of electroactive solutes in solid PEO-LiCF₃SO₃ when acetonitrile vapor was present.⁽⁵⁾



Ultimately, a plasticized system may absorb enough solvent to reach a highly swollen gel condition. If ions are present, their mobilities can then approach those in the liquid plasticizer, with the polymer acting as an inert matrix rather than a conduction medium. Experimentally, the demarcation between the plasticized polymer and the incipient gel may not always be apparent. Either condition usually is acceptable from a device standpoint if it provides adequate conductivity, solid or semisolid handling characteristics, and thermal stability over the required operating and storage temperature ranges.

The absorption of water and its influence on ionic conduction in PEO-LiBF₄ films were investigated previously in this laboratory.⁽⁶⁾ Although conductivities as high as $3 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ were attained, water in excess of the composition LiBF₄·3H₂O proved to be unstably absorbed. Under constant vapor pressure, much of the excess water escaped spontaneously from the film within a few minutes after its absorption, and a corresponding drop in conductivity to $\sim 2 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$ occurred.

The present paper reports on an effort to produce a more stable plasticized or gelled electrolyte with PEO and a low-volatility organic additive. Preferred characteristics of the



plasticizer included a high dielectric constant to promote ionic conduction and a wide liquid temperature range to reduce the tendency for evaporation or for phase separation on cooling. Graham *et al.* had observed extensive swelling of a PEO-type polymer, without syneresis, by propylene glycol (PG) and several other organic liquids.⁽⁷⁾ In that study, water fell within another group of solvents that also caused swelling initially but underwent syneresis, or spontaneous separation of liquid, on standing. The polymer in that investigation was prepared by crosslinking poly(ethylene glycol) of average molecular weight near 6,000 in the presence of 2-ethyl-2-hydroxymethylpropane-1,3-diol. In addition to its favorable swelling effect on the crosslinked polymer, PG has a relatively high dielectric constant of 32 at 20°C and a very wide liquid temperature range (f.p. -60°C; b.p. 188°C).⁽⁸⁾

With that background, we selected PG for investigation as a plasticizer of polymer-salt films prepared from high molecular-weight (MW 4,000,000) linear PEO. The use of thin films rather than bulk polymer specimens permitted much faster acquisition of data. The salts included KCl, which does not complex with PEO in the solvent-free condition, and LiCl and LiBF₄, which are known to form definite PEO complexes.⁽¹⁾ The uptake of PG from the vapor phase was monitored by recording the near-IR absorbance as a function of time, and the film resistance was measured at intervals in the same experiment. Although major swelling and exceptional conductivity were not found, the data



revealed some interesting contrasts in polymer electrolyte behavior with single and mixed salt components.

EXPERIMENTAL

The PEO, average MW 4,000,000, was from Polysciences, Inc.; the propylene glycol (1,3-propanediol) was a J. T. Baker product (b.p. 186-189°C), and the lithium fluoroborate was from Ozark-Mahoning. The other chemicals were reagent grade.

Casting solutions were prepared by dissolving the PEO and salt in boiling water and stirring until a uniform mixture was obtained. A typical solution contained 0.04 g PEO per gram of water. After cooling to room temperature, the liquid solution was manually cast onto a 2.54-cm diameter single-crystal sapphire disk bearing two parallel metal-strip electrodes, 1.27 cm wide and 0.06 cm long, and separated by 0.318 cm. The electrodes, consisting of sputtered gold electroplated with silver, were located off-center on the disk to provide an unobstructed region of the film on which an infrared spectrum could be recorded.

The film sample was predried under a blanketing stream of nitrogen and then placed, with a blank sapphire disk, in a double infrared (IR) cell which had four sapphire windows and a gas inlet and outlet.⁽⁶⁾ The cell was mounted in a Beckman DK-



2A spectrophotometer for in situ determination of conductance and IR absorbance. The measurements were made at room temperature, near 23°C, unless otherwise noted.

After final drying of the film by nitrogen, the gas stream was diverted through a container of PG, thereby introducing the glycol to the electrolyte through the vapor phase. Although the vapor pressure of PG is only 0.11 torr at 23°C, the uptake of glycol was evident almost immediately in the IR absorbance and increased conductance of the film.

Infrared spectra that included the OH band near 3 μm were recorded at times from about 5 to 450 min following admission of the glycol. The absorbance at 3.05 μm was taken as a measure of the glycol content of the film. Calibration at this wavelength relative to pure liquid glycol was done by obtaining spectra on weighed glycol films approximately 4 μm thick, held by surface tension between two of the polished sapphire disks. An absorbance of 1.00 unit corresponded to 0.336 mg/cm^2 of liquid PG.

Film conductances were measured at 1,000 hz. Most of the data were obtained by an ac current method in which the film sample with metal electrodes was connected in series with a variable sine-wave voltage source and an oscilloscope that had 1 megohm input resistance. Since the impedance was nearly



all resistive, the total resistance of the sample plus 1 megohm was found simply from the ratio of the peak-to-peak voltage output of the source to the peak-to-peak current measured on the oscilloscope. Resistances up to 10^9 ohms were determined in this way. At a later stage, when a Genrad 1689M Digibridge impedance meter became available, that instrument was used to verify the ac current method and to characterize several of the electrolyte films. Data from the impedance meter at 1,000 hz are reported in terms of the resistance in a parallel resistance-capacitance equivalent of the film sample.

Film thicknesses in the dry state were estimated two ways: (a) By use of a measuring microscope, with limited exposure of the film to air, and (b) by calculation from the lithium content of the film, assuming the dry film density to be 1.2 g/cm^3 (6). Lithium was determined by atomic absorption on a solution prepared by dissolving a known area of film in water after completion of the measurements. The dry-film thicknesses ranged from 29 to 81 μm .

RESULTS AND DISCUSSION

Table 1 gives the film compositions and thicknesses and summarizes results of the conductance measurements. Total absorbances and resistances of films containing the various salts are plotted as functions of time in Fig. 1-4.



That absorbance (A_t) includes the loss of light due to the glycol plus any residual loss due to scattering.

Absorption of PG. For KCl and LiCl films, the absorption process appeared to be essentially normal, with gradual uptake of PG on exposure of the film to the glycol vapor. However, the data did not fit a simple diffusion model. Adapting the treatment of Anderson and Saddington for diffusion in a slab of finite thickness,⁽⁹⁾ one would expect, at long times, a linear increase of absorbance with time. Such plots (not shown) for the films containing KCl or LiCl were nonlinear.

The behavior of the LiBF_4 preparations was more complex, as Fig. 3 indicates. In that case, the glycol content of the film reached a maximum at 1 hr and then gradually decreased toward a constant level. This spontaneous loss occurred under constant partial pressure of PG in the gas phase. It closely resembles the loss of water from films of $\text{PEO-LiBF}_4\text{-H}_2\text{O}$ or salt-free $\text{PEO-H}_2\text{O}$ reported previously.⁽⁶⁾ Such losses apparently are caused by increased ordering of the polymer. Surprisingly, the loss was not observed in PEO films containing both LiBF_4 and KCl. Fig. 4 represents such a case. The curve for absorbance vs time shows an inflection near 50 min and then continually rises to approach a constant value. It is not yet clear what initiates restructuring of the polymer or why this was not observed when KCl or LiCl was present as a major component of the film.



The PEO-salt films in the present study actually underwent very little swelling. For example, Film 8 at 120 min contained only 0.10 g PG per gram of PEO, based on the IR absorbance calibration with liquid PG. In contrast, the crosslinked PEO gel of Graham *et al.* absorbed as much as 4.5 times its own weight of PG.⁽⁷⁾ This major difference in affinity for PG could be due to steric differences in the polymers or to the presence of hydrogen-bonding OH groups in the gel of the crosslinked polymer.

Conductance. The measured film resistance ranged from 1×10^9 ohms in solvent-free PEO-salt preparations to 1.2×10^6 ohms in Film 8, which contained both LiBF_4 and KCl , after a 2-hr exposure to PG vapor. When the sample geometry is taken into account, the latter resistance corresponds to a bulk conductivity of approximately $4.0 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$.

The conduction behavior depended on the type of salt present. This is evident in Fig. 5-7, where the measured conductances ($1/R$) are plotted as functions of $(A_t - A_0)$. A_t is the absorbance at $3.05 \mu\text{m}$ at time t and A_0 is the initial absorbance, or apparent absorbance, before introduction of the glycol. With KCl , the conductance was low and not highly dependent on the PG concentration. That behavior could result if all of the salt dissolved at an early stage and only a



moderate decrease in ion pairing or increase in mobility occurred on dilution. The LiCl films showed a stronger dependence of conductance on the PG content, which could be represented by three linear segments on the log-log plots in Fig. 5. At this stage, it would be speculative to associate all of these changes in slope with specific mechanisms. However, the steepest rises observed with LiCl (Film 2) and LiCl + KCl (Film 7) may have signified a flooded condition in which the polymer layer was essentially shorted by a liquid electrolyte phase.

The spontaneous loss of PG from PEO-LiBF₄-PG films is manifested in peculiar shapes of the conductance-absorbance plots in Fig. 6. Within the times of the experiments, this system clearly was in a different regime from those of the KCl, LiCl, or combined LiBF₄-KCl preparations. With LiBF₄ only, the conductivity stabilized, after several hours, at 0.2 to 1×10^{-5} ohm⁻¹cm⁻¹, depending on the film sample.

Film 8, Fig. 7, attained the highest conductivity observed, 4.0×10^{-5} ohm⁻¹cm⁻¹ without PG loss or a drastic increase in the slope of $(1/R) \text{ vs } (A_t - A_0)$. This conductivity would be adequate for an electrochromic display cell if the electrolyte layer thickness did not exceed 10 μm ; it is within a useful range, but is not outstanding, for such a high-rate device. It may be compared with the value of 2.7×10^{-5} ohm⁻¹cm⁻¹ at 30°C reported



by Shriver and co-workers for a solid complex of LiCF_3SO_3 and a methoxyethoxyethoxide phosphazene polymer (MEEP), without a plasticizer.⁽²⁾

CONCLUSIONS

High-molecular-weight PEO-salt films plastized with a small proportion of PG attained a room temperature conductivity of at least $4 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$.

The PG uptake in these systems was much less than the PG uptake reported in the literature for PEO crosslinked in the presence of 2-ethyl-2-hydroxymethylpropane-1,3-diol.

The complication of spontaneous PG loss occurred in PEO- LiBF_4 -PG films, but the loss was prevented or inhibited if the film contained KCl in addition to LiBF_4 . Films in the PEO-KCl-PG or PEO- LiCl -PG systems did not lose PG spontaneously under the conditions of this investigation.

**ACKNOWLEDGMENT**

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TABLE 1. CHARACTERISTICS OF PEO-SALT-PG FILMS

FILM	COMPOSITION ^a	DRY THICKNESS		SELECTED DATA		
		MICROSC (μm)	Li ANAL (μm)	TIME ^b (MIN)	CONDITION ^c	MOLE RATIO ^d PG/Li
1	(PEO) _{5.4} KCl	-	-	114	HIGHEST MEAS CONDUCTANCE	-
2	(PEO) _{3.6} LiCl	-	-	33 75	1ST CHANGE OF SLOPE 2ND CHANGE OF SLOPE	-
3	(PEO) _{3.6} LiCl	-	-	20 45	1ST CHANGE OF SLOPE 2ND CHANGE OF SLOPE	-
4	(PEO) _{3.8} LiBF ₄	-	39	106 348	MAX ABSORBANCE FINAL ABSORBANCE	0.048 0.044
5	(PEO) _{3.8} LiBF ₄	-	29	89 240	MAX ABSORBANCE FINAL ABSORBANCE	0.30 0.25
6	(PEO) _{4.1} LiBF ₄	51	81	80 450	MAX ABSORBANCE FINAL ABSORBANCE	0.057 0.023
7	(PEO) _{4.1} LiBF ₄ (KCl) _{0.70}	38	40	10 30	1ST CHANGE OF SLOPE 2ND CHANGE OF SLOPE	0.093 0.34
8	(PEO) _{4.1} LiBF ₄ (KCl) _{0.70}	41	51	35 120	1ST (ONLY) CHANGE OF SLOPE HIGHEST MEAS CONDUCTANCE	0.054 0.34

CONDUCTIVITY^e
(OHM⁻¹CM⁻¹) $\times 10^6$ ~ 0.4
~ 0.5
~ 1
~ 1
~ 2
1.9^f
2.2^f
9.3^f
9.6^f
1.9
1.9
0.86
3.3
3.1
40^aIN THIS TABLE, PEO DENOTES THE ETHYLENE OXIDE REPEATING GROUP.^bFOLLOWING INTRODUCTION OF PG.^cFIGURE 5, 6 OR 7.^dFROM IR ABSORBANCE AND Li ANALYSIS.^eBASED ON APPROXIMATE THICKNESS OF 50 μm FOR FILMS 1-3; ON Li ANALYSIS FOR FILMS 4-8.^fMEASUREMENTS WITH IMPEDANCE METER.

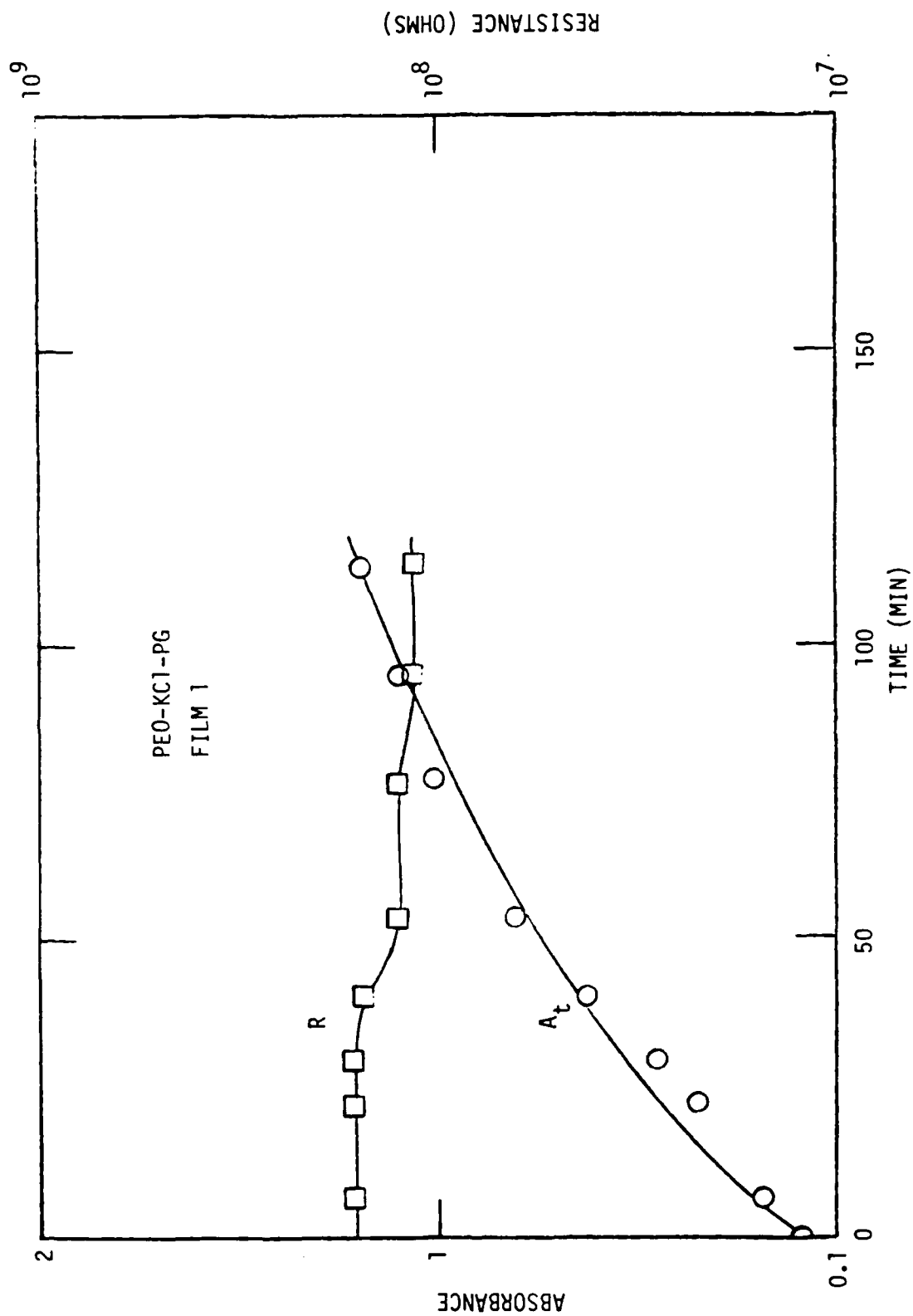


Figure 1. Variation of Resistance and Absorbance of PEO-KCl Film During Exposure to PG Vapor

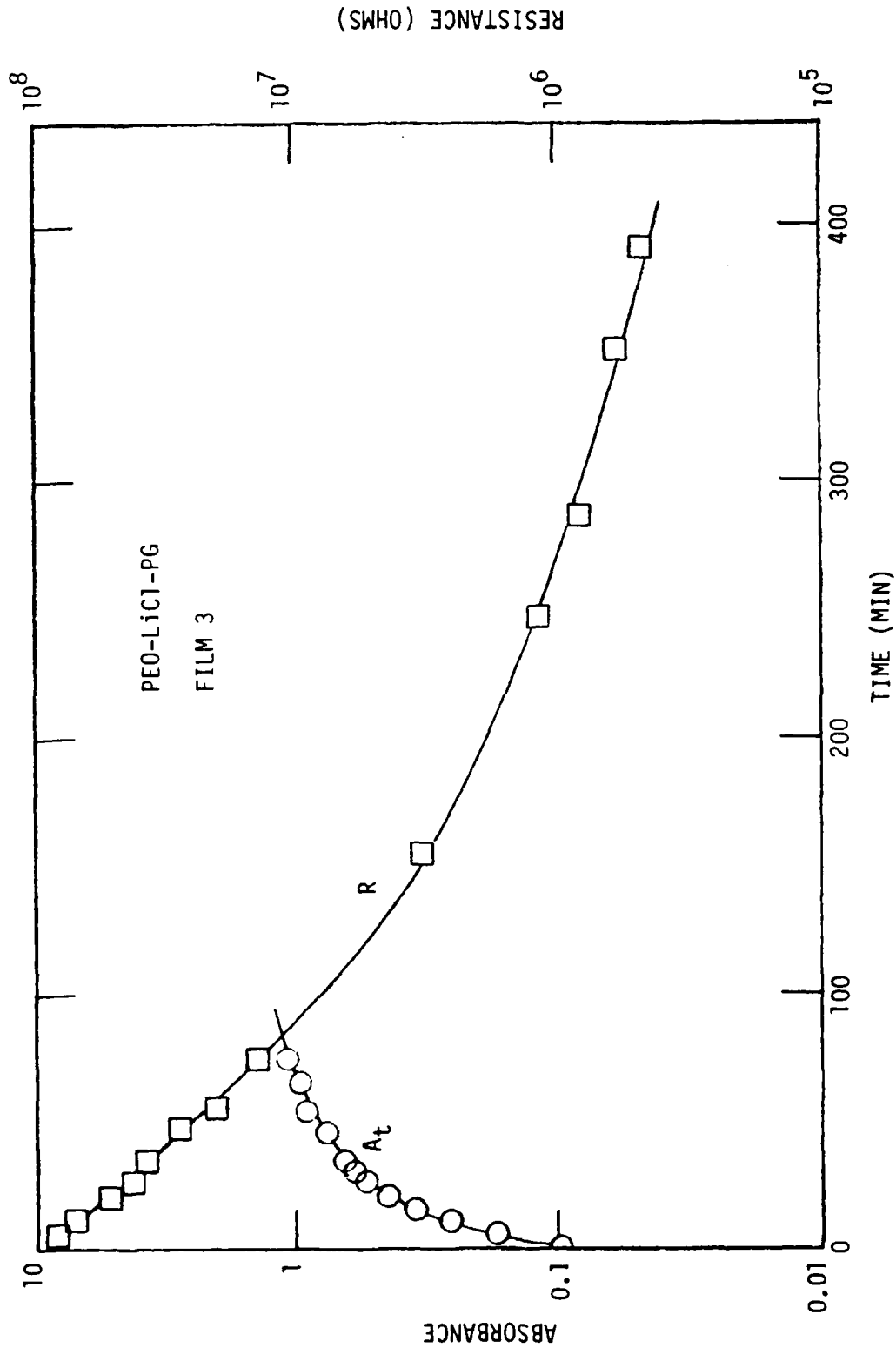


Figure 2. Variation of Resistance and Absorbance of PEO-LiCl Film During Exposure to PG Vapor

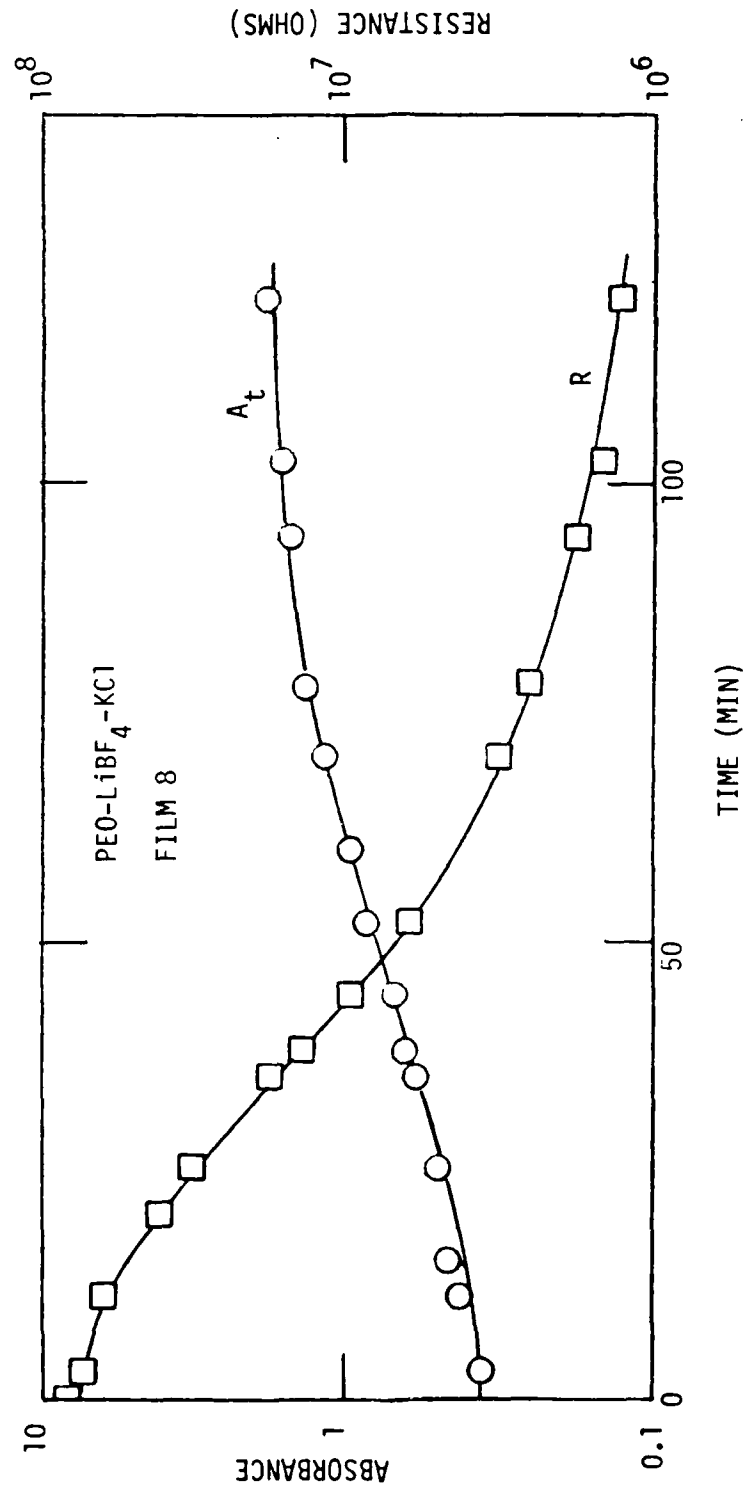


Figure 4. Variation of Resistance and Absorbance of PEO-LiBF₄-KCl Film During Exposure to PG Vapor

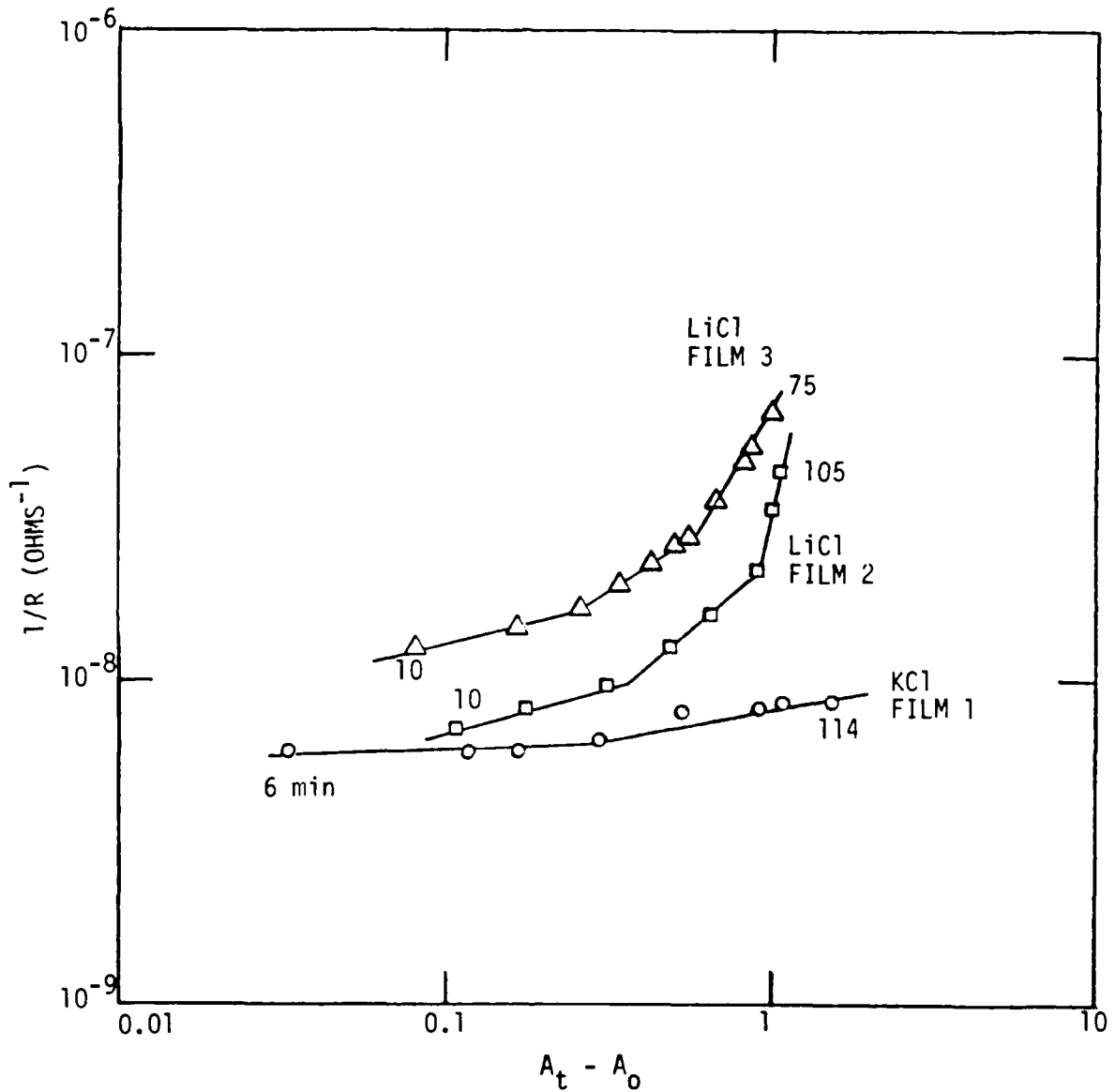


Figure 5. Dependence of Measured Conductance on Absorbance at Various Times in PEO-KCl and PEO-LiCl Films Exposed to PG Vapor

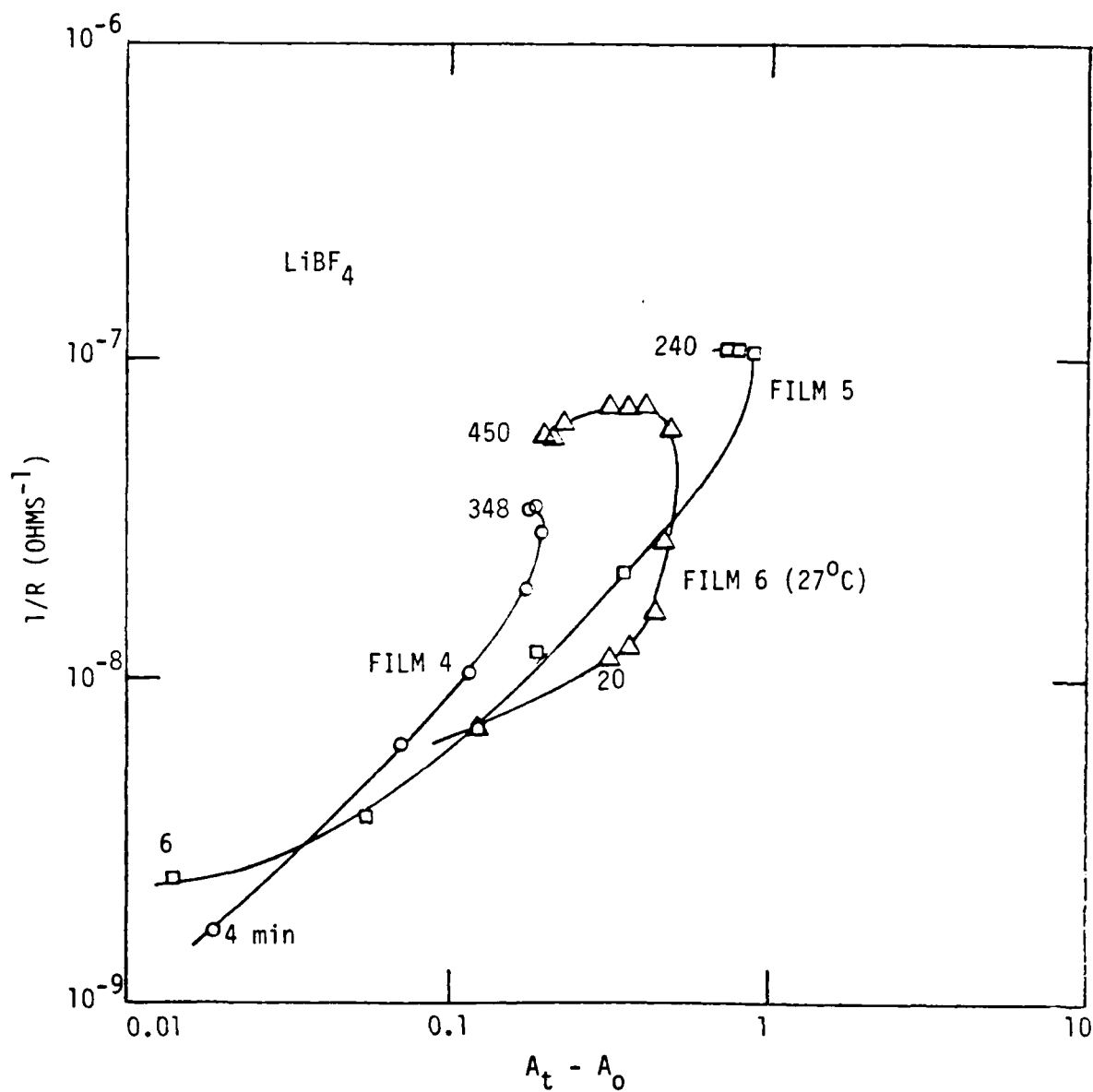


Figure 6. Dependence of Measured Conductance at Various Times in PEO- LiBF_4 Films Exposed to PG Vapor

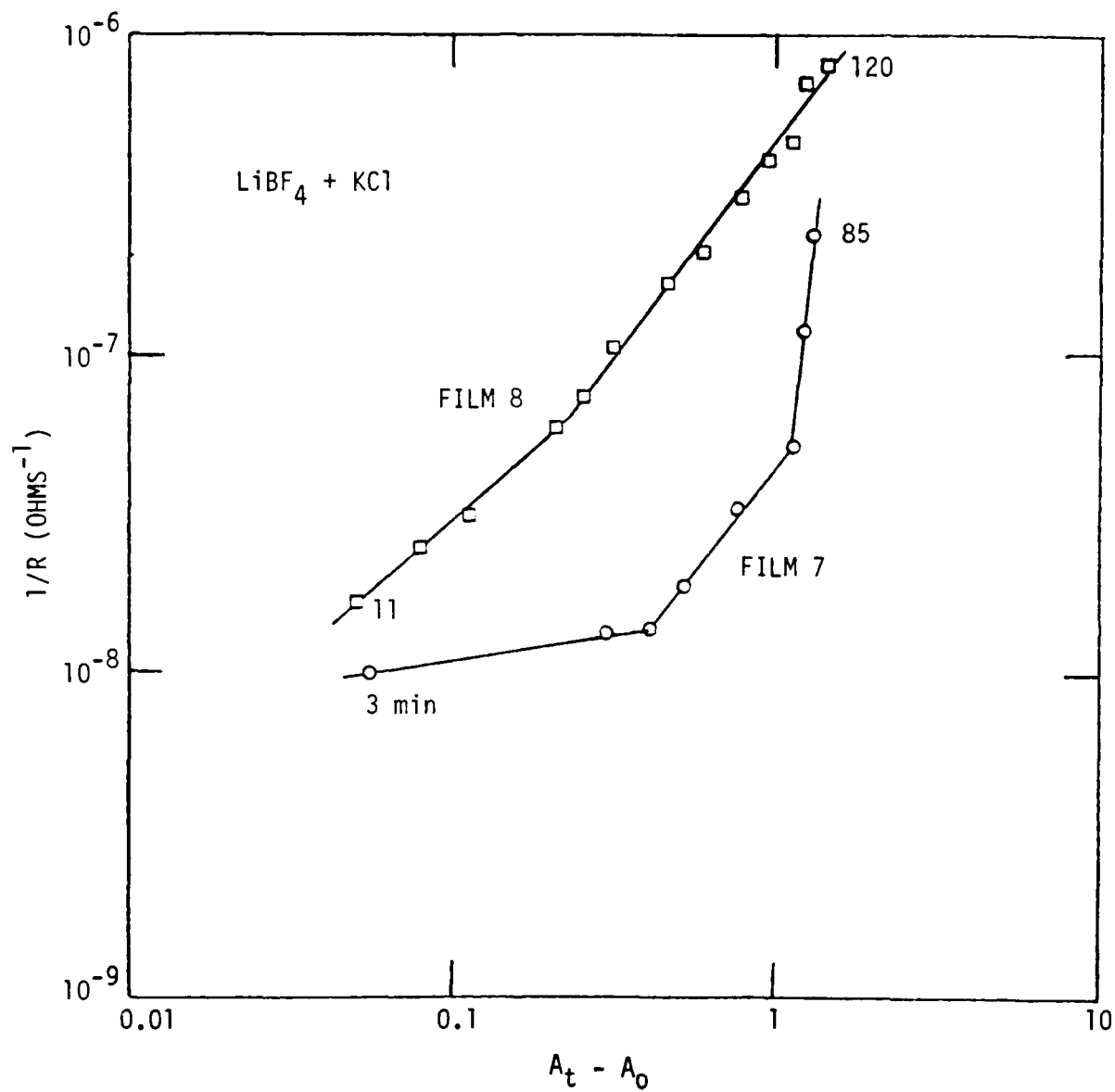


Figure 7. Dependence of Measured Conductance at Various Times in $\text{PEO-LiBF}_4\text{-KCl}$ Films Exposed to PG Vapor

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